MATHCAD FILE-WORKING SHEET FOR SIMULATION OF SURFACE REGENERATIVE EC' catalytic mechanism (EC'=Electrochemical Mechanism Coupled with Regenerative Chemical Reaction) in SQUARE-WAVE VOLTAMMETRY

Rubin Gulaboski, Valentin Mirceski

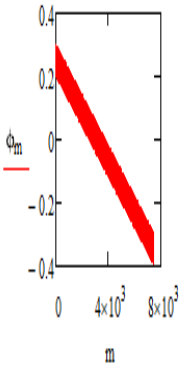
$Es := 0.25$ $\Delta E := 0.004$ $Esw := 0.05$

$m := 1..\frac{0.6}{\Delta E}\cdot 50$

$$relativenpot_m := \left[\left(ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right)\cdot\Delta E + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - \Delta E\right]$$

$\phi_m := Es + Esw - relativenpot_m$

$\alpha := 0.5$



$F := 96500$ $n := 2$ $R := 8.314$ $T := 273.15$ $i := 1..1$

$\gamma_i := 10^{0.85+i\cdot 0}$ $\lambda_i := 10^0$

$k := 1..\frac{0.6}{\Delta E}\cdot 50$ $M_{k,i} := e^{-\frac{\gamma_i}{50}\cdot(k-1)} - e^{-\frac{\gamma_i}{50}\cdot(k)}$

$\log(\gamma_i) =$ 0.85 $\gamma_i =$ 7.0795

$\log(\lambda_i) =$ 0

$\Phi_m := \frac{n\cdot F}{R\cdot T}\cdot\phi_m$

$$I_1 := \lambda_1\cdot e^{-\alpha\cdot\Phi_1}\cdot\left[1+\lambda_1\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)\cdot R^{-1}\right]^{-1}$$

$$I_m := \lambda\cdot e^{-\alpha\cdot\Phi_m}\cdot\left[1-\left(1+e^{\Phi_m}\right)\cdot R^{-1}\cdot\sum_{j=1}^{m-1} I_j\right]\cdot\left[1+\lambda\cdot e^{-\alpha\cdot\Phi_m}\cdot\left(1+e^{\Phi_m}\right)\cdot R^{-1}\right]^{-1}$$

Povrsinska reakcija

$$\Psi_{1,i} := \frac{\lambda_1\cdot e^{-\alpha\cdot\Phi_1}}{1+\lambda_1\cdot e^{-\alpha\cdot\Phi_1}\cdot\left(1+e^{\Phi_1}\right)\cdot\frac{M_{1,i}}{\gamma_i}}$$

Ox(ads)+ ne = Red(ads)

Red(ads) + Y = Ox(ads) ---this is the regenerative step

SURFACE CATALYTIC EC' mechanism in Square-wave voltammetry

λ is dimensionless kinetic parameter related to electrode reaction
ks is rate constant of electrode reaction
kc is catalytic rate constant
γ is dimensionless catalytic parameter related to regenerative reactions
α is electron transfer coefficient
Es is starting potential
Ef is final potential
dE is potential step
Ψ is symbol for dimensionless current
Em is cathodic potential ramp in cyclic voltammetry
En is anodic potential ramp
Mk is a numerical integration factor
τ is duration of potential steps
D is diffusion coefficient of Ox and Red

Remark: there is no diffusion in this model

$$I_m := \lambda \cdot e^{-\alpha \cdot \Phi_m} \cdot \left[1 - \left(1 + e^{\Phi_m}\right) \cdot R^{-1} \cdot \sum_{j=1}^{m-1} I_j\right] \cdot \left[1 + \lambda \cdot e^{-\alpha \cdot \Phi_m} \cdot \left(1 + e^{\Phi_m}\right) \cdot R^{-1}\right]^{-1}$$

$$\Psi_{1,i} := \frac{\lambda_i \cdot e^{-\alpha \cdot \Phi_1}}{1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_1} \cdot \left(1 + e^{\Phi_1}\right) \cdot \frac{M_{1,i}}{\gamma_i}}$$

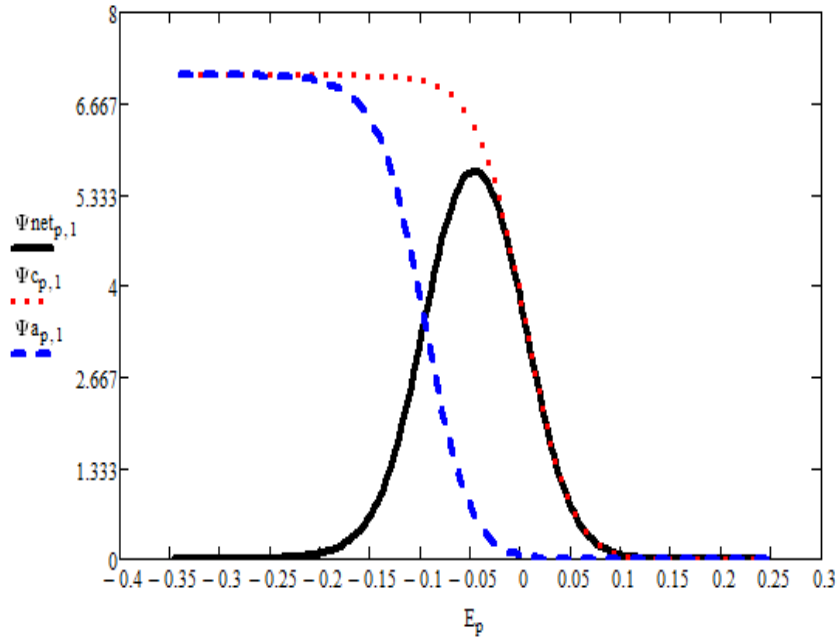
$$\Psi_{m,i} := \frac{\lambda_i \cdot e^{-\alpha \cdot \Phi_m} \cdot \left[1 - \frac{1 + e^{\Phi_m}}{\gamma_i} \cdot \sum_{j=1}^{m-1} \left[\Psi_{j,i} \cdot M_{(m-j)+1,i}\right]\right]}{1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \cdot \left(1 + e^{\Phi_m}\right) \cdot \frac{M_{1,i}}{\gamma_i}}$$

Katalitcka povrsinska reakcija

$$p := 1 .. \frac{0.6}{\Delta E} - 1 \qquad E_p := Es - p \cdot \Delta E$$

$$Ia_p := I_{50 \cdot p + 25} \qquad Ic_p := I_{(p+1) \cdot 50} \qquad Inet_p := Ic_p - Ia_p$$

$$\Psi a_{p,i} := \Psi_{50 \cdot p + 25, i} \qquad \Psi c_{p,i} := \Psi_{(p+1) \cdot 50, i} \qquad \Psi net_{p,i} := \Psi c_{p,i} - \Psi a_{p,i}$$



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